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RESEARCH DIVISION

Washington Research Center, Clarksville, Maryland 21029

June 26, 1967

National Aeronautics and Space Administration  
George C. Marshall Space Flight Center  
Huntsville, Alabama 35812  
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Gentlemen:

Attached is the Eighth Monthly Progress Report for NASw-1415  
for the period April 1 through April 30, 1967.

  
B. Grushkin  
Senior Research Chemist

BG:jk

FACILITY FORM 602

N67-85077

(ACCESSION NUMBER)

(THRU)

5

(PAGES)

(CODE)

CR-87044

(NASA CR OR TMX OR AD NUMBER)

(CATEGORY)

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Synthesis of Linear, Double Chain, Ladder Polymers from  
Substituted Tetracosphonitriles

Monthly Progress Report No. 8  
April 1 through April 30, 1967

By

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Contract No. NASw-1415  
SC No. 10-9197  
Control No. 21-055-001(003)

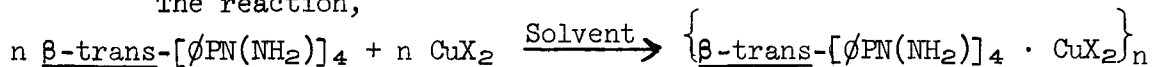
## ABSTRACT

During the final month of the contract the emphasis was placed upon the preparation and characterization of the coordination polymers of  $\beta$ -trans- $[\phi\text{PN}(\text{NH}_2)]_4$  with various copper and cobalt salts. A study of the reaction conditions necessary to obtain 1:1 adducts was made varying the solvent, reactant ratios, transition metal salt, reaction temperatures, and reaction time. Polymeric material was obtained without the elimination of ammonia and the transition metal could be quantitatively removed from these polymers with sequestering agents leaving impure  $\beta$ -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ . Heating the 1:1 coordination polymer leads to deammoniation and a different polymer with the transition metal coordinated in part with the phosphonitrile ring nitrogens. Thermal studies on both types of polymers were conducted with a thermogravimetric balance. The pattern of thermal degradation is similar to that observed for the ladder polymers obtained from  $\beta$ -trans- $[\phi\text{PN}(\text{NH}_2)]_4$  except in the polymers that contain transition metal sulfates. In this specific case, the weight loss attributable to phenyl-phosphorus bond-cleavage occurs at temperatures  $50^\circ$  to  $100^\circ\text{C}$  higher than the degradation temperature of the other polymers.

## DISCUSSION

### I. Copper Coordination Polymers with $\beta$ -trans- $[\phi\text{PN}(\text{NH}_2)]_4$

The reaction,



has been conducted in a variety of solvents; methylene chloride, tetrahydrofuran, dimethoxyethane, acetonitrile, and chlorobenzene. Attempts to prepare adducts with cupric chloride, cupric sulfate, cupric sulfate monohydrate, and cupric sulfate pentahydrate in varying stoichiometric ratios to phosphonitrilic cyclic have been made. The combination of equimolar amounts of  $\text{CuCl}_2$  and PN cyclic in THF has been the most satisfactory, leading to 1:1 polymeric adducts in high yields.

A summary of the preparations conducted during this period is shown in the following table.

Transition Metal Salt	Ratio of Salt to $\beta$ -trans- $[\phi\text{PN}(\text{NH}_2)]_4$	Solvent	Yield of $\text{CHCl}_3$ Sol. Polymer	Empirical Formula of Polymer
$\text{CuSO}_4 \cdot \text{H}_2\text{O}$	10:1	$\text{CH}_2\text{Cl}_2$	0%	--
$\text{CuSO}_4 \cdot \text{H}_2\text{O}$	1:1	THF	0%	--
$\text{CuSO}_4 \cdot \text{H}_2\text{O}$	1:1	Glyme	70%	--
$\text{CuSO}_4 \cdot \text{H}_2\text{O}$	1:1	$\text{CH}_3\text{CN}$	80%	$\text{P}_4\text{N}_6\text{C}_{30}\text{H}_{29}(\text{CuSO}_4 \cdot \text{H}_2\text{O}) \cdot 4$
$\text{CuSO}_4$	1:1	$\text{CH}_3\text{CN}$	<15%	$\text{P}_4\text{N}_6\text{C}_{30}\text{H}_{29}(\text{CuSO}_4 \cdot \text{H}_2\text{O})$
$\text{CuCl}_2$	1:1	$\text{CH}_3\text{CN}$	86%	$\text{P}_4\text{N}_7\text{C}_{24}\text{H}_{28}(\text{CuCl}_2) \cdot 6$
$\text{CuSO}_4$	1:1	THF	0%	--
$\text{CuSO}_4$	1:1	Glyme	50%	$\text{P}_4\text{N}_8\text{C}_{24}\text{H}_{28}(\text{CuSO}_4) \cdot 3$

CuSO <sub>4</sub> ·5H <sub>2</sub> O	10:1	C <sub>6</sub> H <sub>5</sub> Cl	0%	--
CuCl <sub>2</sub>	1:1	THF	90%	P <sub>4</sub> N <sub>8</sub> C <sub>26</sub> H <sub>28</sub> (CuCl <sub>2</sub> ) <sub>1</sub>
CuCl <sub>2</sub>	1:1	THF	96%	P <sub>4</sub> N <sub>7</sub> ·6C <sub>26</sub> H <sub>35</sub> (CuCl <sub>2</sub> ) <sub>1</sub>
CuCl <sub>2</sub>	1:1	Glyme	70%	P <sub>4</sub> N <sub>5</sub> C <sub>21</sub> H <sub>24</sub> (CuCl <sub>2</sub> ) <sub>0.75</sub>

It was concluded from this study that the best solvent is THF when the salt is CuCl<sub>2</sub>. Adducts are formed in acetonitrile and dimethoxyethane (glyme) when the salt is CuSO<sub>4</sub>·H<sub>2</sub>O, but these materials do not contain one copper per cyclic. Partial deammoniation occurs in acetonitrile.

A clue to the manner in which the copper salt was incorporated into the polymer was obtained by attempts to remove it with sequestering agents. Treating the polymer with water had no effect, but agitation with 0.01N HCl caused the polymer to slowly lose the copper salt, leaving impure but easily identifiable β-trans-[ $\phi$ PN(NH<sub>2</sub>)]<sub>4</sub>. Treatment of the polymer with aqueous 1.0N base did not lead to loss of the copper salt. Three sequestering agents, the trisodium salt of nitrilo triacetic acid (N(CH<sub>2</sub>COONa)<sub>3</sub>), imidoacetic acid (HN(CH<sub>2</sub>COONa)<sub>2</sub>), and ethylene diamino tetraacetic acid, disodium salt, were stirred with the polymer in chloroform solution. In each case the removal of copper salt was rapid and the material remaining was impure β-trans-[ $\phi$ PN(NH<sub>2</sub>)]<sub>4</sub>.

The polymeric adducts could be thermally deammoniated by heating to approximately 190°C. No careful measurements of the amount or rate of ammonia evolution were made, but the polymeric residue was soluble in chloroform and approximately the same green color as the material with four NH<sub>2</sub> groups on each cyclic. The infrared pattern of this material showed a new absorption band at 1150 cm<sup>-1</sup> which is typical of phosphonitrilic cyclics with a metal coordinated with the ring nitrogens. Treatment of this deammoniated polymer with EDTA, disodium salt, did not lead to as rapid a removal of copper salts as had been observed with the original polymer  $\left[ [\phi\text{PN}(\text{NH}_2)]_4 \cdot \text{CuCl}_2 \right]_n$ .

## II. Cobalt Coordination Polymers with β-trans-[ $\phi$ PN(NH<sub>2</sub>)]<sub>4</sub>

Additional quantities of the β-trans-[ $\phi$ PN(NH<sub>2</sub>)]<sub>4</sub>·CoCl<sub>2</sub> polymer were prepared in yields of 49% and 76%. The polymers analyze for one tetramer per CoCl<sub>2</sub> unit and various chloroform soluble fractions had molecular weights from 1100 to 4600. When treated with an aqueous solution of the trisodium salt of nitrilo triacetic acid, the cobaltous chloride was quantitatively removed leaving impure β-trans-[ $\phi$ PN(NH<sub>2</sub>)]<sub>4</sub>. Upon heating, the polymer evolved ammonia, and an elemental analysis of the resulting polymer, 19.6%N, 13.3%N, 43.3%C, 3.2%H, 9.8%Cl and 8.3%Co, indicated the empirical formula was  $\phi_4\text{P}_4\text{N}_4(\text{NH})_2 \cdot \text{CoCl}_2$ . This polymer did not react with an aqueous solution of the sequestering agent, the trisodium salt of nitrilo triacetic acid.

### ANTICIPATED WORK

To conclude the contract, the thermal behavior of the various deammoniated polymers will be investigated to determine if there are significant improvements over regular ladder polymers.

MANPOWER EXPENDED

The following breakdown shows the cumulative man-hours expended to date:

	<u>T h r o u g h</u>		
	<u>February</u>	<u>March</u>	<u>April</u>
Principal Investigator	201	238	295
Department Director	76	85	94
Senior Chemist	1678	1958	2474
Technician	2032	2184	2404
Analytical Chemist	45	53	
Analytical Technician	20	22	

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